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DIOXIN MONITORING PROGRAM

STATE OF MAINE

2001

BY

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DEPARTMENT OF ENVIRONMENTAL PROTECTION

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Acknowledgements

Successful collection of the samples was accomplished directly by DEP staff, assisted by the Penobscot Indian Nation on the Penobscot River. The Department of Inland Fisheries and Wildlife and Atlantic Salmon Commission also assisted in collecting samples and providing nets. Bjorn Lake, a graduate student at the University of Maine, conducted the SPMD studies. Close cooperation with the the Environmental Chemistry Laboratory at the University made the analytical results much better.

EXECUTIVE SUMMARY

The goal of Maine's Dioxin Monitoring Program, established in 1988, is "to determine the nature of dioxin contamination in the waters and fisheries of the State". Charged with administration of the program, the Department of Environmental Protection (DEP) is required to sample fish once a year below no more than 12 bleached pulp mills, municipal wastewater treatment plants, or other known or likely sources of dioxin. DEP is required to incorporate the results of all studies into a report to the Joint Standing Committee on Natural Resources by March 31 of the following year. Costs of sample collection and analysis are assessed to the selected facilities. DEP is advised by the Surface Water Ambient Toxic (SWAT) Monitoring Program Technical Advisory Group in implementation of the program.

The primary objective of the Dioxin Monitoring Program is to monitor dioxin in fish for assessment of ecological and human health. A second objective is to measure trends, progress toward reduction in environmental concentrations, and effectiveness and need for further controls. A third objective is to determine if bleached kraft pulp mills are discharging dioxin into Maine rivers, which is prohibited as of December 31, 2002 by the dioxin law of 1997 [38 MRSA section 420(2)(I)] The final test is that fish (or surrogate) downstream have no more dioxin than fish (or surrogate) upstream of a mill’s discharge, the ‘above/below' test.

In 2001, the Dioxin Monitoring Program continued development of a suitable 'above/below' fish test. Intensive monitoring of bass and suckers on the Androscoggin, Kennebec, and the Penobscot rivers was conducted. Small juvenile bass were sampled again for the second year but liver and caged mussel sampling were abandoned. In addition, as part of DEP's SWAT monitoring program, semi-permeable membrane devices (SPMDs) were deployed as potential surrogates for the fish test.

Fish Consumption Advisories

Based on data through 1999, the Maine Bureau of Health revised the fish consumption advisories in August 2000 (Appendix 1). There is a 'General Consumption Advisory for All Inland Surface Waters due to Mercury Contamination'. Also there are more restrictive 'Specific Freshwater Fish Consumption Advisories' for the Androscoggin River, Kennebec River below Madison, the Penobscot River below Lincoln, Salmon Falls River below Berwick, and Sebasticook River (including East and West branches) due to PCBs and dioxins. An advisory on lobster tomalley was continued from 1994 along the entire coast of Maine due to dioxins and PCBs.

Findings of the 2001 Program

1. **Concentrations of 2378-TCDD (TCDD) or dioxin toxic equivalents (DTEh) increased slightly in 8 species/station samples, decreased slightly in 8 other species/station samples, and remained the same in 22 species/station samples compared to 2000. Most of those that increased were more similar to concentrations in 1998-99 than to those of 2000.**

2. **Concentrations of DTEH exceeded the Bureau of Health's Fish Tissue Action Level for cancer (FTALc=1.5 ppt) in trout and bass above Rumford, and in suckers below Rumford and Jay on the Androscoggin River, in brown trout below Hinkley on the Kennebec River, and in eels from the below Brewer on the Penobscot River.**

3. **The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in higher levels of total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level at other locations as well. Sources of**

PCBs are unknown but likely include long-range transport and atmospheric deposition.

4. **Concentrations of 2378-TCDD (TCDD) and DTEh in all fish samples collected below bleached kraft mill discharges to the Androscoggin River, Kennebec River, and Penobscot River, were significantly greater than those at reference stations unimpacted by point sources.**

5. **Concentrations of TCDD and DTEo in white perch from Androscoggin Lake were significantly greater, although marginally so, than in game fish from all other lakes (n=8) or river reference stations that have been sampled. However, concentrations of TCDD and DTEh were lower than in previous years, continuing what appears to be a declining trend since the lake was first sampled in 1996. Concentrations were also lower than those in fish from the Androscoggin River.**

6. **There was no significant difference in TCDD, TCDF or DTEh in bass or suckers from above and below SAPPI Westbrook's paper mill, but at both stations concentrations remain significantly higher than at any other reference station.**

7. **Since the development of the Above/Below test began in 1997, over 78 tests have been conducted for different dioxins, species, tissue types, and other surrogates in an attempt to develop a test powerful enough to accurately measure any differences above and below a mill. Juvenile and mature bass, sucker filets and semi-permeable membrane devices show the most promise, depending on station and year, and will be tested again in the 2002 program.**

INTRODUCTION

Maine's Dioxin Monitoring Program (DMP), established in 1988, has been amended and reauthorized through 2002 by the Maine legislature. The goal of the program is "to determine the nature of dioxin contamination in the waters and fisheries of the State". Charged with administration of the program, the Department of Environmental Protection (DEP) is required to sample fish once a year below no more than 12 bleached pulp mills, municipal wastewater treatment plants, or other known or likely sources of dioxin. The Department is also required to sample sludge once a quarter from the same facilities.

The primary objective of the DMP is to monitor dioxin in fish for assessment of ecological health and of human health. The data are used by the Maine Bureau of Health (BOH) to determine the need for any Fish Consumption Advisories to protect human consumers of fish from certain Maine rivers. The data are also used by DEP and other state and federal agencies in determining impacts of discharge of dioxin on wildlife species.

A second objective is to continue monitoring at some historical stations to measure trends. Trends are followed to measure progress toward reduction in environmental concentrations and effectiveness and need for further controls.

A third objective, to identify sources and magnitude of dioxin discharges, received new emphasis in 1997 when the Maine legislature enacted LD 1633 "An Act to Make Fish in Maine Rivers Safe to Eat and Reduce Color Pollution". The key requirement is that ‘a (bleach kraft pulp) mill may not discharge dioxin into its receiving waters’ [38 MRSA section 420(2)(I)]. Interim tests that concentrations of TCDD in effluent from the bleach plant must be below EPA’s method 1613 nominal detection limit (10 ppq) by July 31, 1998 and TCDF must be below the same detection limit by December 31, 1999 have been achieved. As the final test, by December 31, 2002 fish below a bleached kraft pulp mill have no more dioxin than fish above the mill, the so-called "above/below (A/B) fish test". Although the DMP has successfully detected differences above and below discharges in past years, as the amount of dioxin discharged is reduced, the DMP has been modified to allow an enhanced ability to detect smaller differences with known statistical confidence.

The monitoring program is coordinated with other ongoing programs conducted by the Department, US Environmental Protection Agency (EPA), or dischargers of wastewater. The proposed annual monitoring plan must be submitted to the Surface Water Ambient Toxic (SWAT) monitoring program Technical Advisory Group (TAG), created under 38 MRSA section 420-B, for review and advice. The selected facilities must be notified of their inclusion in the proposed program at least 30 days prior to submittal to the TAG. The Department must incorporate the results of all studies into a report due the Natural Resources Committee by March 31 of the following year. A draft of the report is reviewed by the TAG before completion of the final report. Costs of sample collection and analysis are assessed as a fee to the selected facilities. Payment of

the fees is a condition of the waste discharge license granted by the state for continued operation and discharge of wastewater to waters of the State. However, if the selected facility is a publicly owned treatment works (POTW), then the fees may be assessed to the known or likely industrial generator of dioxin and payment will not be a condition of the waste discharge license of the POTW.

Due to continuing controversy over the effects of dioxin on human and ecological health, the US Environmental Protection Agency (EPA) announced that in 1991 it would begin a thorough scientific reassessment of dioxin. EPA proposed that the process would be open to the public and consequently held several meetings to share information and receive comments. A draft report was issued in 1994 and subsequent review in 1995 by EPA's Science Advisory Board called for revisions of some chapters. Revised drafts published in 2000 indicate that dioxin may exhibit reproductive and developmental effects, immuno-toxic effects, neuro-toxic effects, and cancer. In addition, the reports find that concentrations of dioxin in the environment have decreased since the 1970S. Also 'EPA currently estimates that the amount of dioxin in tissues of the general human population closely approaches within a factor of 10, the levels at which adverse effects might be expected to occur'. In March 2001 EPA's Scientific Advisory Board published its draft review of EPA's new revisions and is divided on whether or not dioxin is a carcinogen, but does believe EPA has underestimated non-cancer effects. The SAB also does not agree that there is enough evidence to support EPA's statement about current body burdens and probable adverse health impacts.

DEP has determined, from fish collected since 1984, that concentrations of dioxins in fish from locations unaffected by local sources are less than 0.15 ppt, while concentrations in fish below those sources of dioxin are consistently greater than that. Consequently, as one method of determining known or likely sources of dioxin, a Fish Monitoring Threshold (FMT=0.15 ppt) is used by DEP to determine stations that will be retained in the annual program.

For informing the public about potential risk from consuming fish contaminated with dioxin and dioxin-like compounds, the BOH publishes fish consumption advisories. These advisories are based on a comparison of a Fish Tissue Action Level (FTAL) for dioxin toxic equivalent (DTE) concentrations with the 95th percentile upper confidence limit on the mean DTE in fish

tissue. Should a tissue concentration exceed an FTAL, a fish consumption rate (e.g., #meals per month) which is unlikely to result in deleterious effects is determined. Two FTALs have been derived for evaluating potential deleterious effects from exposure to dioxins and dioxin-like compounds. Both FTALs were developed using standard USEPA risk assessment methods (EPA 1997). For potential carcinogenic effects associated with long-term exposure, BOH has developed a FTALc of 1.5 ppt, while for reproductive and developmental effects potentially arising from shorter exposure durations, BOH has developed a FTALr of 1.8 ppt (Frakes, 1990). The FTALr for reproductive and developmental effects is relevant to women of childbearing age, pregnant women, and lactating women. The FTALs are compared to the concentration of DTE in edible portions of the fish, skinless filet data. Where whole fish data are reported, the DTE concentration is divided by a factor of 3.5, determined from previous studies with white suckers, to estimate skinless filet concentration. In this report all comparisons with DTE in fish are made with FTALc, since that is the lower of the two and protective of both effects.

PROGRAM DESIGN

The primary emphasis of the 2001 program was to collect fish samples from the appropriate stations and species from each river such that accurate, complete, and current data are available to assess impact to wildlife and human consumers. The program design included sampling at least one station below each major source to document trends and sampling of historic stations that showed dioxin above the FMT, whether or not any fish consumption advisories were issued. Finally the program was modified to evaluate the ability to detect minimum significant differences of the appropriate magnitude for the above/below fish test.

The 2001 program was initially drafted by DEP according to the objectives listed above and sent to participating facilities for comment in early May and to the SWAT TAG later in the month. The workplan was discussed finalized at the SWAT TAG meeting on July 3, 2001.

In 2001 all stations were monitored for ecological and/or human health assessment and trends (Table 1). At least 5 game fish (bass or other important species) were collected from each station and analyzed as skinless fillets. At some

Table 1. 2001 Dioxin Monitoring Program- Stations, facilities, and species

STATION	FACILITY	SPECIES
Androscoggin R		
Gilead	Meadwestvaco	bass, sucker, trout
Rumford	Mead	bass, sucker
Riley	IP	bass, sucker
Liv Fls(Otis imp)	IP	bass, sucker
Turner (GIP)	Mead & IP	bass
Lisbon Falls	Mead & IP	bass
Androscoggin Lake	Mead & IP	bass, sucker,w perch
Kennebec R		
Norridgewock	SAPPI Somerset	bass, sucker, trout
Fairfield	SAPPI Somerset	bass, sucker, trout
Sidney	KSTD	bass, trout
Penobscot R		
Woodville	Lincoln P&P	bass, sucker
S Lincoln	Lincoln P&P	bass, sucker
Milford	Fort James Co	bass, sucker
Veazie	Fort James Co	bass, sucker
Orrington	Brewer	eel
Presumpscot R		
Windham	SAPPI Westbrook	bass, sucker
Westbrook	SAPPI Westbrook	bass, sucker
Salmon Falls R		
S Berwick	Berwick Sewer Dist.	bass
Sebasticook R		
W Br Palmyra	Town of Hartland	bass

stations, the fish were analyzed individually, while at other stations, fish were combined into composite samples (Table 2)in order to minimize cost and remain under the monetary cap.

In order for DEP to accurately determine whether or not there is a discharge of dioxin from a mill, for the Above/Below (A/B)Fish Test, the minimum significant difference (MSD) that

can be determined with acceptable statistical probability needs to be relatively small and relevant to background concentrations. Ideally the MSD should be established before the test at some absolute value or fraction of the background concentration. During debate

Table 2. 2001 Dioxin Monitoring Program, Sample Sizes and Type

STATION	SMB	sSMB	WHS	OTHER	N
Androscoggin R					
Gilead				5 RBT	5
Rumford Point	5		2C5		7
Rumford	5		2C5		7
Riley	10	10	10C2		30
Livermore Falls	10	10	10C2		30
Turner (GIP)	5	2C5			7
Lisbon	5				5
Androscoggin L	2C5*		2C5	2C5 WHP	6
Kennebec R					
Norridgewock	10		10	5 BNT	25
Fairfield	10		10	5 BNT	25
Sidney	5			5 BNT	10
Penobscot R					
Woodville	10		10		20
S Lincoln	10		10		20
Milford	5		2C5		7
Veazie	5		2C5		7
Bangor				2C5 EEL	2
Presumpscot R					
Windham	5		2C5		7
Westbrook	5		2C5		7
Salmon Falls R					
S Berwick	2C5				2
W Br Sebasticook R					
Palmyra	5				5
* 2 composites of 5 fish each					
sSMB= small bass				total	234
				limit	235

in the legislature, a MSD of 10% of the background concentration was proposed as a goal by DEP. This would work for TCDF and DTE, where measurable quantities are determined, but not for TCDD, where background concentrations are generally below detection. For TCDD, the detection level (0.05-0.1 ppt wet weight) itself was proposed to serve as the goal. Although initially thought to be achievable, results from 1997-2000 showed that MSDs were generally not close to the 10% goal. The best results were with filets of mature bass or suckers or with whole juvenile bass, depending on the year and station.

Therefore, in 2001 parts of the DMP was repeated to gather data for a second year to see if MSDs from earlier years could be repeated or improved (Table 2). For the A/B test, 10 samples of both species were collected at each of 3 pairs of stations. At the Androscoggin River in Riley and Livermore Falls, filets from 10 legal sized smallmouth bass were collected to be analyzed as individuals. In addition 20 male white suckers were collected to be analyzed as 10 composites of 2 fish each for the suckers, in order to increase the sample volume and decrease the detection limit. For the second year, 10 juvenile bass were also collected to be analyzed individually at both stations. At Norridgewock and Fairfield on the Kennebec and at Woodville and South Lincoln on the Penobscot River, filets from 10 legal sized smallmouth bass and 10 suckers were also collected to be analyzed as individuals. At all other Above/Below stations, ten white suckers were captured and combined into 2 composites of 5 fish each. Trout were analyzed as individuals at all stations.

All samples were analyzed for all 2378-substituted dioxins and furans. Station locations along with specified fish species are shown in Table 1. Station location maps show exact locations of collections (Appendix 6).

At stations affected by a single discharger, sampling will continue yearly until there are at least two consecutive cycles for each species where dioxin is below the FMT and is not increasing. At stations affected by more than one discharger where fish concentrations are not below the FMT, each discharger will continue to be included in the annual sampling program until enough evidence has been gathered to demonstrate that dioxin is no longer present in the discharge in significant quantities. Such evidence must be at least 8 consecutive sludge analyses, equally distributed over all seasons for a minimum of two years, that show no 2378-TCDD

(TCDD) detected at a suitably low detection level, (2) full congener analysis of sludge for all 2378 substituted dioxins and furans, (3) other pertinent information such as process changes, changes in hook-ups that show reductions in the level of dioxins and furans being discharged to insignificant levels.

The preferred sampling time is late in the summer when fish are likely to be most contaminated after being exposed to higher concentrations of dioxin during low river flows and after significant growth has occurred. At some locations there has been a problem collecting enough fish later in the summer. Here sampling began in mid-May to try to insure that a suitable sample was collected. These stations were also visited after the beginning of July. If fish were captured during the later period, those samples were submitted for analyses. Otherwise, the fish collected during the early period were used. Sampling at other stations began in July (Appendix 8).

As part of DEP’s SWAT monitoring program, semi-permeable membrane devices (SPMDs) were deployed in 2 experiments in the Androscoggin River (described in a later section).

SAMPLING PROCEDURES

Fish were collected by DEP with assistance of state agencies and the Penobscot Indian Nation. Upon capture, fish were immediately killed, weighed and measured, rinsed in river water, wrapped in aluminum foil with the shiny side out, labeled, and placed in a cooler on ice for transport to the DEP lab. Chain-of-custody forms were used to record all field information and document all transfers. In the lab, all fish samples were frozen and later transported whole to the Senator George J. Mitchell Center for Environmental and Watershed Research (formerly the Water Research Institute) at the University of Maine for analysis. All other procedures generally followed EPA's Sampling Guidance Manual for the National Dioxin Study (July 1984). A laboratory log was kept for an inventory of samples in the lab at any time and final disposition.

Most of the facilities in the program already sample sludge or effluent as part of their Maine Sludge Spreading Permit or Waste Discharge License or Federal NPDES permit. Data from those programs provide adequate information about sources of

dioxin. Therefore, no additional sludge samples were collected as part of this program. Effluent data are also used when available to indicate sources and any trends.

CALCULATIONS

In this report, DTE are shown as a range with non-detects calculated at zero (DTEo) and at the detection limit (DTEd) as a mean for all samples of a given species at each station (Table 3). For comparison with the FMT and FTALc, and comparison between years and stations, DTEh were used as calculated using non-detects at 1/2 the detection limit. The upper 95th percentile confidence limit (UCL) was used for these comparisons, consistent with the policy of the BOH. In some cases (reference stations) DTEo were also discussed since those were below the FMT while DTEh exceeded the FMT, which shows the importance of low detection limits and the treatment of non-detects. For the other stations both DTEo and DTEh were above the FMT, and DTEo were not discussed.

A related issue is that of EMPCs, estimated maximum possible concentrations. Some compounds, particularly hydroxydiphenyl ethers (DPEs), are coextracted with furans. Various steps have successfully been taken to minimize these interferences, but some DPEs remain. In this report, EMPCs were treated as non-detects.

Statistical analyses of differences in TCDD and DTEh between stations were performed using the either the t-test or non-parametric Mann-Whitney test. In this report only differences that are statistically significant at p=0.05 will be reported as significant. Trends were determined using Kendall’s tau, a rank-order correlation statistic, for the period 1997-2001. The minimum number of data points needed is 4, and with only 5 for this period, there were no significant trends at p=0.05. There were some trends significant at P=0.10 described as marginal in the following discussions.

RESULTS AND DISCUSSION

Most of the samples of fish targeted in the initial workplan were collected (Appendix 2). Mean concentrations of TCDD and DTEh for each species and station for the last 5 years are shown in Table 3 while earlier data are in Appendix 10. A description of fish collected and results for each sample location with respect to the objectives of the program is

discussed below. For each station there are (1) a comparison of DTEh 95th upper confidence level (95UCL) to the Fish Tissue Action Level cancer endpoint (FTALc=1.5 ppt in filets, 5.25 in whole suckers), (2) a comparison of TCDD and DTEh with those at reference stations, (3) a discussion of trends in TCDD and DTEh in fish and (4) a discussion of TCDD and TCDF in sludge or wastewater as an indicator of trends in discharges. Following discussion of each station is a section of the Above/Below test comparing the efficacy of many different tests.

TCDD in fish have normally been below detection (0.1 ppt) in river reference stations (except the Presumpscot at Windham) and lakes (except Androscoggin Lake) tested. Trace amounts of DTEh (0.2-0.3 ppt, less than 10% of the FTALc) at these reference stations are likely due to the ubiquitous atmospheric deposition.

Androscoggin River

Gilead- Five rainbow trout and one brown trout were collected near Peabody Island in Gilead, while five bass and the ten white suckers were caught further downsteam at Rumford Point (Appendix 7). As both stations are downstream of the American Pulp and Paper Co's bleached kraft mill in Berlin, New Hampshire, they are therefore not true reference stations unimpacted by direct discharge of dioxin. Both stations are upstream of all Maine mills on the river and are considered the same station relative to point sources.

DTEh in rainbow trout, brown trout, bass and suckers were 178%, 171%, 102%, 66% of the FTALc respectively (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in higher levels of total toxic equivalents (TTEh) that further exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. Every year measured, TCDD and DTEh in fish have been significantly higher at this station than in fish from reference stations in Maine (Table 3). There was no significant trend for the period 1997-2001 for any species. The American Tissue mill in Berlin, New Hampshire, has reported to have switched to elemental chlorine free (ECF) bleaching (chlorine dioxide) in 1994. The mill closed in 2001.

Rumford- Five smallmouth bass and ten white suckers were collected from the river reach from just below the discharge

from MeadWestvaco Corporation's bleached kraft pulp and paper mill in Rumford downstream about 4 miles to Dixfield (Appendix 7). Concentrations of DTEh in the bass and in the suckers were 55% and 45% of the FTALc respectively (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in higher levels of total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in the suckers as well (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. TCDD and DTEh concentrations were significantly greater than reference stations on other Maine rivers (Table 3). There was no significant trend for bass during the period 1997-2001, and suckers were not evaluated. No sludge data have been reported since 1989. Concentrations of both TCDD and TCDF have been reported below variable detection levels in final effluent since 1993 and below a 10 ppq detection limit in bleach plant effluent since 1998 up through 2000, the latest data are available (Appendix 4).

Riley- Ten legal sized smallmouth bass, ten juvenile bass, and 20 male white suckers were collected from the river above the Riley Dam, about 19 miles downstream of MeadWestvaco Corporation and upstream of International Paper Company's discharge (Appendix 7). Concentrations of DTEh in the legal sized bass and suckers were 67% and 150% of the FTALc respectively (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. DTEh were significantly greater than reference stations on other Maine rivers (Table 3). There was no significant trend for the period 1997-2001 for either species.

Livermore Falls- Ten legal sized smallmouth bass, 10 juvenile smallmouth bass, and 20 male white suckers were captured in the Otis Impoundment, approximately 2 miles downstream of the discharge from International Paper Company's Jay mill (Appendix 7). Concentrations of DTEh in the legal sized bass and suckers were 91% and 127% of the FTALc respectively (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that further exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. TCDD and DTEh were significantly greater than reference stations on other Maine rivers (Table 3). There was no significant trend for the period 1997-2001 for either species. There are no new sludge data since 1996, but concentrations of TCDD and TCDF in bleach plant effluent and final effluent are well below EPA's reporting level up through 2000, the latest data are available (Appendix 4).

Auburn-GIP- Five smallmouth bass and ten white suckers were collected in Gulf Island Pond (GIP) near the deep hole at Seagull Island, approximately 30 miles downstream of International Paper Company (Appendix 7). Concentrations of DTEh in the bass and suckers were 51% and 55% of the FTALc respectively (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in higher levels of total toxic equivalents (TTEh) in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. TCDD and DTEh concentrations were significantly greater than reference stations on other Maine rivers (Table

3). There was a marginally significant decline in DTE in bass during the period 1997-2001.

Lisbon Falls- Five smallmouth bass were captured in the Pejepscot Impoundment, approximately 45 miles below International Paper Company (Appendix 7). Concentrations of DTEh were 94% of the FTALc (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in higher concentrations of total toxic equivalents (TTEh) in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. TCDD and DTEh were significantly greater than reference stations on other Maine rivers (Table 3). There was no significant trend for the period 1997-2001 for bass (suckers were not sampled).

Androscoggin Lake

Wayne- Androscoggin Lake in Wayne and Leeds is a 4000 acre 38 foot deep meso-trophic lake with a unique reverse delta at the outlet formed by centuries of periodic backflow from the Androscoggin River via the Dead River into the lake. There is a dam on the Dead River that reduces but does not prevent the backflow into the lake, which usually occurs once or twice every year. Significant amounts of dioxin were found in fish from the lake in 1996, 1998, 1999, and 2000. In 2001, ten smallmouth bass, ten white perch, and ten white suckers were collected from the lake and analyzed as 2 composites of 5 fish each. DTEh were 30%, 35%, and 30% of the FTALc for bass, white perch, and suckers respectively, (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. Concentrations of TCDD and DTEo in white perch were significantly greater than in game fish from all other lakes (n=8) or river reference stations that have been sampled, but the difference was small (Table 3). There was a marginally significant decline in TCDD concentrations in bass during the period 1996-2001. Concentrations were also lower than those in fish from the Androscoggin River.

Kennebec River

Norridgewock- Five brown trout, ten smallmouth bass,and 10 white suckers were collected from the river at Norridgewock

(Appendix 7). Although these locations are downstream of the discharge from Madison Paper Industries discharge in Madison, comparison of dioxin in fish from this station in 1998 and 1999 with that from fish caught at the Kennebec River reference station above Madison previously, showed no significant difference between the two locations. These locations therefore serve both as a reference for the river and the upstream station for the SAPPI Somerset mill.

DTEh in all three species were 28%, 31%, and 26% FTALc, but this was an artifact of relatively high detection limits as shown by DTEo at 3-6% of the FTALc for all three species (Appendix 2). In fact, TCDD and most other congeners that add significantly to the DTE were below detection and therefore the FMT for all samples. TCDF was present in all samples in small amounts. The differences between DTEh and DTEo are much larger at these stations than at any station downstream of point sources on the river, and document the problem of the impact of high detection limits and treatment of non-detects. The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. TCDD and DTEo were similar to those from previous years for this and the Madison station, but TCDF concentrations in bass were higher than ever before. DTEh vary among years due to different detection limits. The trace amount of DTE measured in these fish is likely due to long-range transport and atmospheric deposition from remote sources. This station was also used for additional development of the above/below fish test described in a later section of this report.

Fairfield- Five brown trout, ten smallmouth bass, and ten white suckers were collected from the river between the Shawmut Dam and the I-95 bridge, approximately 7-8 miles below SAPPI Somerset's bleached kraft pulp and paper mill in Skowhegan (Appendix 7). Concentrations of DTEh in bass, brown trout, and suckers were 139%, 51%, and 60% of the FTALc respectively (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that further exceed a Fish Tissue Action Level in these fish (DEP, 2000). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. Concentrations of TCDD and DTEh were significantly greater than those at the reference station at Norridgewock for all three species (Table

3). There was no significant trend for the period 1997-2001 for either species. Effluent data (Appendix 4) and sludge data (Appendix 3) document decreases in discharges over the years especially since early 1997 up to 2000, the latest data are available. Concentrations of TCDD and TCDF are well below the limits of the new law (<10ppq in the bleach plant). This station was also used for additional development of the above/below fish test described in a later section of this report.

Sidney- This station is downstream of Lockwood Dam in Waterville/Winslow which is about 10 miles downstream of the current discharges from SAPPI Somerset in Skowhegan. The Kennebec Sanitary Treatment District discharges about 2 miles downstream of the dam that processes effluent from Huhtamaki, a paper mill. Five brown trout were captured just below the dam and five smallmouth bass were collected about 10 miles below the dam in Sidney. Both of these fish samples are considered to be from the Sidney station since the fish have free movement within this river reach. Concentrations of DTEh in trout and bass were 67% and 49% of the FTALc respectively (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2000). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. Concentrations of TCDD and DTEh in trout and bass were significantly greater than those at the reference station at Norridgewock (Table 3). There was no significant trend for the period 1997-2001 for either species. Sludge data from KSTD in recent years show that TCDD is below 1 ppt, but TCDF and DTEh are occasionally detected at a few ppt documenting the continued discharge of small amounts of dioxin to the river.

Penobscot River

Woodville- Although this station is downstream of Great Northern's pulp and paper mills in Millinocket and East Millinocket, fish collected at this station in 1997 and 1998, had similarly low concentrations of dioxin as the historical reference station at Grindstone on the East Branch, uninfluenced by these mills. Therefore, this station may serve as a reference station for the Penobscot River and the upstream station for Lincoln Pulp and Paper.

Ten smallmouth bass and ten white suckers were collected from this station. Concentrations of DTEh in bass and suckers were 32% and 28% of the FTALc respectively (Appendix 2), but this was an artifact of detection levels and the impact of treatment of non-detects. Concentrations of all congeners that add significantly to DTE were below detection and therefore the FMT, except for small amounts of TCDF. As a result concentrations of DTEo were only 6% of the FTALc for both species. The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Concentrations of TCDD and DTEh were similar to those of past years, but TCDF concentrations were slightly higher than in years past (Table 3).

Winn- As in previous years, at the request of Lincoln Pulp and Paper Company in Lincoln, bass (10) and suckers (5) were captured from the river at Winn, approximately 4 miles below the confluence with the Mattawamkeag River and about 8 miles upstream of the Company's bleached kraft mill in Lincoln. The Mattawamkeag River is thought by the Company to potentially be a source of dioxin downstream of the Woodville station and the Winn station is believed by the Company to be a more appropriate station for the above/below test. Funding for this work was provided by the Company above and beyond the DMP. TCDD was not detected in any sample for either species. DTEh were 29% and 28% of the FTALc for bass and suckers respectively (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Concentrations of all congeners that add significantly to DTE were below detection and therefore the FMT, except for TCDF. As a result concentrations of DTEo were an even smaller percentage (~5%) of the FTALc for both species. Concentrations were similar to those of the Woodville station. Since these results have been variable from year to year but show no trend, they do not support the idea that there is a significant source between the Woodville station and mill. Also since the results and other fish and sediment data collected by the Penobscot Indian Nation are not conclusive and there is no barrier to prevent fish from moving up from below the mill, this station may not be a good reference for the Above/Below fish test.

South Lincoln- Ten smallmouth bass and ten white suckers (Appendix 7) were collected from the river near the boat ramp in South Lincoln, approximately 4 miles downstream of Lincoln Pulp and Paper Company's bleached kraft mill in Lincoln. Concentrations of DTEh in bass and suckers were 60% and 61% of the FTALc respectively (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. Concentrations of TCDD and DTEh were significantly greater than those at the Woodville reference station (Table 3). There were no trends in TCDD or DTE either species for the period 1997-2001. This is interesting since there were decreased discharges from the mill as documented by decreased concentrations of TCDD and TCDF in sludge (Appendix 3) and in effluent since 1997. Reductions in effluent show compliance with the limits of the new law (Appendix 4) as a result of a change in the mill's bleaching process from chlorine based bleaching to primarily oxygen based bleaching in 1999. Full benefit will likely take longer to discern in fish.

Milford- Located at Freese Island near the boat ramp in Costigan, this station is approximately 34 miles downstream of Lincoln Pulp and Paper Company's bleached kraft mill in Lincoln and is the upstream station for the above/below test for the Fort James mill about 5 miles downstream. Five smallmouth bass and five white suckers were captured from this station. Concentrations of DTEh in bass and suckers were both 58% of the FTALc (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. Concentrations of TCDD and DTEh were significantly greater than those at the Woodville reference station (Table 3).

Veazie- Five smallmouth bass and ten white suckers (Appendix 7) were collected from the Veazie Impoundment about 7-8 miles below Fort James' bleached kraft mill in Old Town.
Concentrations of DTEh in bass and suckers were 44% and 38% of the FTALc respectively (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range

transport and atmospheric deposition. Concentrations of TCDD and DTEh were significantly greater than those at the Woodville reference station (Table 3). There was no significant trend for the period 1997-2001 for either species. This is surprising since TCDD and TCDF bleach plant effluent concentrations at the Fort James mill have continued to decline since early 1998 and have met the limits of the new law.

Orrington- Ten eels were collected from an eel fisherman from the river in Orrington, downstream of the Town of Brewer's sewage treatment plant outfall and combined into 2 composites of 5 fish each. The Brewer treatment plant treats wastewater from the Eastern Fine Paper mill which uses pulp made at Lincoln Pulp and Paper Co in Lincoln.
Concentrations of DTEh were 135% of the FTALc (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that further exceed the Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. Concentrations of TCDD and DTEh were significantly greater than those for bass, another top predator, at the Woodville reference station or any other station (Table 3). Concentrations were significantly greater than those in eels from this same location in 1996 but lower than in 2000 perhaps reflecting lower concentrations in Brewer's sludge and effluent or sludge from Lincoln Pulp and Paper and Fort James, have decreased since that time (Appendix 3, 4).

Presumpscot River

Windham- Five smallmouth bass and ten white suckers (Appendix 7) were collected from the Dundee Impoundment in the river in Windham. Concentrations of DTEh in bass were 30% of the FTALc but DTEo were only 6%, documenting the impact of treatment of non-detects (Appendix 2). Concentrations of all congeners that add significantly to DTE were below detection and therefore the FMT, except for small amounts of TCDF. Concentrations of DTEh in suckers were 33% of the FTALc, but unlike in bass, DTEo were significant at 26% of the FTALc, due to significant levels of TCDF. The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. This station has been used as a

reference station for the Presumpscot River since 1993 since there are no known point sources of dioxin upstream. However, concentrations of TCDD, TCDF, PeCDD, PeCDF and DTEh from this station have historically been significantly higher than all other reference stations in the program every year through 1998 (Table 3, Appendix 10). No samples were collected in 1999, and only bass were collected in 2000. DTEo concentrations in bass were lower in 2000 and 2001 than in previous years, but concentrations in suckers in 2001 are not. These results suggest that there are other local sources of dioxin which have not yet been discovered. These concentrations must represent a combination of background from local sources and long range transport and atmospheric deposition from remote sources.

Westbrook Five smallmouth bass and ten suckers (Appendix 7) were collected from the river near the US Route 302 bridge about 1.5 miles downstream of the discharge from SAPPI Westbrook's bleached kraft pulp and paper mill. In 1999 the pulp mill ceased operation and the paper mill now purchases its pulp. 2001 was the second year since then that fish have been monitored. Concentrations of DTEh in bass were 30% of the FTALc although DTE0 was only 6%, documenting the impact of treatment of non-detects (Appendix 2). Concentrations of all congeners that add significantly to DTE were below detection and therefore the FMT, except for small amounts of TCDF. Concentrations of DTEh in suckers were 42% of the FTALc, but unlike in bass, DTEo were significant at 25% of the FTALc, due to significant levels of TCDF. The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). There was no significant trend for the period 1997-2001 for either species, but data are limited. Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. There was no significant difference in TCDD, TCDF, or DTEh concentrations in bass between this station and the Windham station (Table 3). Sample size (n=2) for the suckers was too small to allow a meaningful statistical comparison; however, the mean concentrations were no higher at this station than at the station above for either species. Effluent and sludge data, taken within a few months of the cessation of the pulp mill in 1999 document reduced discharges from the mill (Appendix 3, 4), but there are no newer data.

Salmon Falls River

South Berwick- Four smallmouth bass (Appendix 7) were collected from the Rollinsford Impoundment about 2 miles below the discharge from the Berwick Sewer District's municipal wastewater treatment plant in Berwick, whose discharge is 85% effluent from Prime Tanning Company. DTEh were 52% of the FTALc all bass combined (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. Concentrations of TCDD and DTEh were significantly greater than in fish from previous years at an upstream reference station at Acton, which had concentrations similar to other reference stations in Maine (Table 3, Appendix 10). There was no significant trend for TCDD or DTEh in bass during the 1990s. There are no new sludge or effluent data from the treatment plant to show any changes in discharges. These results document a local source of dioxin to this reach of the river most likely the Prime Tanning discharge.

Sebasticook River

East Branch at Newport- Five smallmouth bass (Appendix 7) were collected from the river just above the County Road Bridge, a popular fishing spot at the inlet to Sebasticook Lake. This station is approximately 2 miles below the Corinna Sewer District discharge, 80% of which was from the Eastland Woolen Mill. This facility treated the waste from the Eastland Woolen Mill in Corinna until 1996, when the mill ceased operation. Since then groundwater and river sediments have been found to be contaminated with a number of pollutants from the mill including dioxin. The site was placed on the National Priorities List of Superfund sites in 1999, and cleanup has begun. This fish sampling was funded by Maine's SWAT monitoring program. Concentrations of DTEh were 61% the FTALc (Appendix 2). Total toxic equivalents (TTEh), the combination of DTEh and dioxin-like PCBS measured in DEP's SWAT program, may result in a further increase in toxic equivalents in these fish (DEP, 2000). Sources of PCBs are unknown but likely include the mill and/or long-range transport and atmospheric deposition. TCDD and DTEh concentrations were significantly lower than when last measured in 1997, but still significantly greater than in fish from the upstream station above the mill at Corinna measured in 1997 also (Table 3). These results document a local source of dioxin to this reach of the river, most likely residues from Eastland Woolen Mill. Measurable

amounts of furan were found in sludge from the Corinna Sewer District for a number of years, although there are no new sludge data since 1996 and no effluent data to show any recent changes in discharge levels (Appendix 3).

East Branch at Detroit- Five smallmouth bass were collected from the river about 10 miles downstream of the Corinna Sewer District's discharge and 5 miles below Sebasticook Lake. This work was funded by Maine's SWAT monitoring program. Concentrations of DTEh were 40% of the FTALc (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2002). Sources of PCBs are unknown but likely include the mill and/or long-range transport and atmospheric deposition. Concentrations of TCDD were similar to those at the County Road Bridge above the lake but lower than those from fish within the lake sampled in 2000. All were sigificantly greater than those in fish from the reference site upstream of the discharge in Corinna in years past (Table 3, Appendix 10). DTEh were lower than those at the other two stations downstream of the mill but were significantly greater than the upstream reference site in past years. This site still shows contamination from the mill, although less so than upstream stations closer to the source.

West Branch at Palmyra Five smallmouth bass were collected from the river near the US Route 2 bridge about 3-4 miles below the discharge from the Town of Hartland, whose effluent is about 85% effluent from Irving Tanning Company, and combined into two samples of five fish each. Concentrations of DTEh were 51% of the FTALc (Appendix 2). The addition of dioxin-like (coplanar) PCBs, measured as part of DEP's SWAT program, to DTEh may result in total toxic equivalents (TTEh) that exceed a Fish Tissue Action Level in these fish (DEP, 2000). Sources of PCBs are unknown but likely include long-range transport and atmospheric deposition. Concentrations of TCDD and DTEh were significantly greater than in fish from the reference site upstream of the discharge in Great Moose Lake in years past (Table 3, Appendix 10). There were no significant trends for TCDD or DTEh during the 1990s. These results document a local source of dioxin to this reach of the river, most likely the Irving Tanning discharge. Although the only effluent sample result reported (1996) showed no detectable amount of dioxin in effluent (Appendix 4), low solubility and high bioconcentration of dioxin make effluent data less meaningful than sludge data. Sludge data from 1989

show measurable levels of TCDF (Appendix 3), but more recent data in 2000 show concentrations below reasonably low detection levels. If these recent data are representative of reduced discharges, concentrations in fish should decrease in the upcoming years, unless there is residual dioxin remaining in the system.

Above/Below Test

The goal in development of a suitably sensitive Above/Below test, is to be able to detect a minimum significant difference (MSD) in dioxin and/or furan concentrations above and below a mill as small as a target value of 10% of background or as small as possible. MSDs are normalized to mean concentrations above the discharge to provide a relative measure, since units and scales are different for different congeners, test types, species, and tissues. Where the concentrations above the mill are below the detection limit, as is the case for TCDD in muscle tissue, the MSD target is an absolute value (0.05-0.1 ppt) rather than a relative one.

Since the development of the Above/Below test began in 1997, tests of TCDD, TCDF, and DTEo on both a wet and lipid weight basis have been conducted in small bass, single and composite large bass filets, bass livers, large and small whole suckers, single and composite sucker filets, single and composite sucker livers, single and 2 composites of SPMDs, and caged mussels, for a total of 78 tests. Up through 2000, juvenile whole bass and/or mature legal sized bass filets showed the lowest MSDs for most samples, although sucker filets occasionally had the lowest MSDs. Consequently, all three were sampled at one or more stations as previously shown (Table 2).

Bass

Ten mature legal sized bass were captured at one pair of stations on each of the Androscoggin (ARY at Riley above and ALV at Livermore Falls below the International Paper Company mill in Jay), Kennebec (KNW at Norridgewock above and KFF at Fairfield below the SAPPI Somerset mill), and Penobscot (PBW at Woodville above and PBL at S Lincoln below Lincoln Pulp and Paper in Lincoln) rivers, essentially repeating studies conducted in 2000. All bass were to be within a 25 mm length range within and between paired stations, which was achieved for the Androscoggin and Penobscot river samples. Due to difficulty in collecting fish, the fish from the Kennebec were

within 60 mm, rather than 25 mm, of each other within each station, but the range was similar between stations. (Appendix 7). All bass were analyzed as individuals.

Concentrations of TCDD and TCDF on both a wet weight and lipid weight basis and DTEh on a lipid weight basis were significantly higher at Livermore Falls below than at Riley above the mill on the Androscoggin River (Appendix 2). MSDs were normalized to the mean concentrations of Norridgewock and Woodville since both staions are downstream of the MeadWestvaco mill in Rumford. MSDs (Table 4) were generally similar to those from 2000 at the Rumford Point-Rumford A/B stations. MSDs were lower for lipid weights than for wet weights, but none were close to the target values.

Concentrations of TCDD and DTEo on both wet and lipid weight basis and TCDF on a lipid weight basis were all significantly higher at Fairfield below than at Norridgewock above the mill on the Kennebec River as in all previous years (Appendix 2). MSDs (Table 4) were generally lower than those in 2000. MSDs were closest to targets for TCDF followed by DTEo then TCDD, and lipid weight based MSDs were lower than wet weight MSDs, although not by much. MSDs were lower than those from the Androscoggin. None of the MSDs met target values, however.

Concentrations of TCDD and DTEo for both wet and lipid and weights and TCDF for wet weight were significantly higher at South Lincoln below than at Woodville above the mill on the Penobscot River (Appendix 2). MSDs (Table 4) were generally higher than in 2000 except for TCDF on a lipid basis. Lipid weight MSDs were lower than wet weight MSDs. Wet weight MSDs were intermediate those from the other two rivers, but lipid weight MSDs were closer to those from the Kennebec. None of the MSDs met target values, however.

Small Bass

Since small fish of a given species at a station are younger than much larger fish, they generally have lower body burdens of contaminants such as dioxin. In addition, younger fish generally have higher growth rates and uptake of contaminants that may reflect current ambient contaminant levels better than older fish that may have residues from years past. And small fish tend to have smaller home ranges, therefore may be more representative of local conditions than larger fish which may move to different areas within the year. All of these may result in less variation in concentrations and decrease MSDs.

To examine this proposition, in 1999 we collected small suckers from the Kennebec River at Norridgewock (KNW)and Fairfield (KFF). Interestingly, MSDs were higher for the small suckers than for the larger suckers for TCDD, TCDF, and DTEo both on a wet and lipid weight basis. Since, in studies conducted beginning in 1997, MSDs were often lower for large bass than for large suckers, in 2000, small bass, rather than small suckers, were collected from these same stations (Appendix 7). Results were mixed with small bass giving lower MSDs for some measures but not for others.

The study was repeated in 2001. Small (juvenile) smallmouth bass were collected from Riley and Livermore Falls, the same stations on the Androscoggin River as were the mature bass. Concentrations of TCDD and DTEo were significantly higher at Riley, above the mill, than at Livermore Falls below the mill, on a lipid weight basis, but there were no other differences between stations. This may have been the result of the fact that the fish at Riley were, however, significantly larger than those captured at Livermore Falls. This is the opposite from that observed on the Kennebec in 2000, where concentrations in small bass below the mill were significantly higher than in fish above the mill for all measures. The 2001 Androscoggin River juvenile bass MSDs were slightly lower than those for large bass for TCDD, TCDF and DTEo (Table 4). Lipid normalized values were lower than wet weight values. MSDs were lower on a wet weight basis and higher on a lipid weight basis than those in small bass from the Kennebec in 2000. Nevertheless, MSDs were still much higher than the targets.

Suckers

At the same pair of stations on the Androscoggin River, namely Riley and Livermore Falls, 20 mature male suckers were captured and the filets combined into 10 composites of 2 fish each. All suckers were within a 50 mm length range within and between stations (Appendix 7). Concentrations of TCDF on both a wet and lipid weight basis and DTEo on a lipid weight basis were significantly higher in fish at Riley above the mill than at Livermore Falls below the mill, (Appendix 2). MSDs were lowest for TCDF, followed by TCDD, and then DTEo in order (Table 4). MSDs were lower for TCDD but higher for TCDF and DTEo on both a wet and lipid weight basis than in bass. Lipid weight based MSDs were lower than wet weight MSDs, but no MSDs were close to the goal.

From the Norridgewock and Fairfield stations on the Kennebec, ten suckers were captured and the filets analyzed individually. All suckers were within a 50 mm length range within and between stations (Appendix 7). Concentrations of TCDD, TCDF, and DTEo were significantly higher at Fairfield below the mill than at Norridgewock above the mill. MSDs were lowest for TCDF, followed by TCDD, and then DTEo in order and lower on a lipid weight basis than on a wet weight basis (Table 4). MSDs were higher than in bass except for TCDD on a lipid weight basis. MSDs were lower than those for fish from this site in 2000. No MSDs were close to the goal.

Ten large suckers were captured from the Penobscot River at Woodville (PBW) above and at S Lincoln (PBL) below Lincoln Pulp and Paper in Lincoln. All suckers were within a 25 mm length range within and between stations (Appendix 7). All were analyzed as filets. Concentrations of TCDD, TCDF, and DTEo were significantly higher at South Lincoln than at Woodville on a wet and lipid weight basis. MSDs were lowest for TCDF on a wet weight basis but for DTEo on a lipid weight basis and lower on a lipid weight basis overall (Table 4). MSDs were higher than in bass except for TCDD and DTEo on a lipid weight basis. MSDs were also higher than in suckers from the Kennebec except for TCDD and DTEo on a lipid weight basis. MSDs were lower than in this river on 2000, but still not close to the target values.

SPMDs (SEMI-PERMEABLE MEMBRANE DEVICES)

Semipermeable membrane devices (SPMDs) are passive integrative sampling devices which combine membrane diffusion and liquid-

liquid partitioning to concentrate low to moderate molecular mass hydrophobic compounds from water (Huckins et al, 1996). Made of low-density polyethylene lay-flat tubing (2.5 cm wide by 91.4 cm long), containing a thin film of neutral triolein and placed inside stainless steel canisters, SPMDs are deployed in the waterbody where they accumulate contaminants until retrieved.

SPMDs have some features that give them advantages over monitoring contaminants in fish. SPMDs can be deployed in water to accumulate single, pulsed, or continuous contaminant releases over time. SPMDs are anchored to sample at specific locations, thereby avoiding any question of origin of contaminants caused by fish movement. SPMDs do not change function under stress, unlike gills of fish. There are no biotransformations or elimination like that in fish. And accumulation of contaminants does not occur by the same process of uptake in fish, thereby potentially limiting their use to accumulation in a relative sense. When deployed in Maine Rivers for approximately a month, SPMDs are able to sequester enough dioxin/furans for quantification by HRGC/HRMS (Shoven, 2001). SPMD uptake rates have been determined for dioxin/furans in order to calculate dissolved water concentrations (Rantalainen et al, 2000).

There are, however, a number of environmental factors, such as water temperature, biofouling, dissolved organic carbon (DOC), suspended solids, and flow velocity that affect the uptake kinetics of SPMDs. Assuming isotropic exchange kinetics, permeability reference compounds (PRCs) can be added to the SPMD prior to deployment to calibrate the rate change of dioxin/furan uptake caused by environmental conditions (Huckins et al., 2002)

In order to assess the potential of SPMDs to determine if mills are discharging dioxin, DEP has funded studies at the University of Maine Environmental Chemistry Laboratory (formerly the Water Research Institute) since 1999 through the Surface Water Ambient Toxics (SWAT) program. In 1999, the focus was development and refinement of field and laboratory techniques by deploying the SPMDs in the nearby Penobscot River for 3 one-month trials and then retrieving them for laboratory analysis. In 2000, two deployments were made in the Androscoggin River to investigate the effect of time and duration of deployment on biofouling. An above/below trial was also made in both the Androscoggin and Kennebec rivers.

2001

In 2001 the goals were as follows:

1. Validate the deployment scheme and analytical method developed in 2000.
2. Increase the sample size for more statistical power.
3. Decrease the variability between samples to lower the minimal statistical difference and improve the sensitivity of the A/B test.
4. Compare the results from 2000 with 2001.

Site Location

The SPMD field deployments for 2001 were above and below the MeadWestvaco Mill in Rumford from 7/13/01 to 8/10/01 and the International Paper Mill in Jay from 9/22/01 to 10/20/01 on the Androscoggin River. The GPS determined latitude-longitudes for the sites were:

Site	Latitude (DegMinSec)	Longitude (DegMinSec)
Upstream Rumford	N44*31′04″	W70*33′05″
Downstream Rumford	N44*30′10.5″	W70*23′53.3″
Upstream Jay	N44*28′42.4″	W70*16′18.7″
Downstream Jay	N44*29′06.2″	W70*12′13.8″

The Rumford site was chosen to compare the SPMD results from 2001 with those from 2000 at that site. Originally, both 2001 deployments were going to be at the Rumford site. However, due to a shutdown of the MeadWestvaco mill in September, the second deployment was downstream above and below the International Paper mill at Jay. The below sites were a sufficient distance below the mills to ensure proper mixing of the effluent so the dioxin/furans river concentrations were assumed to be at equilibrium.

Deployment Scheme

The Rumford deployment scheme used an elaborate system of surface buoys, ropes and anchors to submerge the SPMD-filled canisters (Shoven, 2001). The system was developed so the canisters would remain approximately 3 feet under the water surface regardless of the water level making sure the canisters avoided contact with the sediment. The deployment

consisted of 40 SPMDs in 8 canisters submerged by two buoy systems at each site. Upon retrieval of the SPMDs, one buoy system at the upstream site had been vandalized by one of the buoys being punctured. Those 20 SPMDs had been resting on the bottom for an unknown amount of time. Due to the difficulties at Rumford, the deployment scheme was changed for Jay. In an effort to avoid vandalism, submerged milk jugs were used as floats to keep the canisters upright at ~10 feet above the sediment with a water depth of ~15 feet. There were four sets of submerged milk jugs with two canisters and 10 SPMDs at each site. No vandalism occurred. However, at the upstream site, 3 sets of milk jugs lost buoyancy and six canisters with 30 SPMDs were found near the sediment. The sediment at this site was sand and gravel; therefore, there was probably no contamination of dioxin from the sediments. For each site, appropriate measures were taken to ensure no contamination during transport, deployment, and retrieval. Also, attached to one canister at each site was a HOBO temperature logger to monitor the hourly water temperature throughout the deployment.

Laboratory Methods

All SPMDs and deployment canisters are purchased from Environmental Sampling Technologies, St. Joseph, MO. All standards are purchased from Cambridge Isotope Laboratories, Andover, MA. All solvents are GC-resolve grade.

The Rumford samples were analyzed according to the 2000 procedural method (Shoven, 2001). The procedure consisted of external washing of the SPMD to remove any periphytic growth followed by an injection of carbon-labeled dioxin/furan and PCB standards to accurately quantify the congeners using the isotope dilution method outlined in EPA Method 1613 (Telliard, 1994). After spiking and drying, the samples underwent a two-stage 24 hour dialysis with 150 ml of hexane at sub-ambient temperatures (~18 C). The dialysates of two SPMDs were then combined into one composite sample to make an N=20 composite samples for each site. The samples were cleaned up using acidified silica gel slurry to hydrolyze any remaining lipid after dialysis. Gel permeation chromatography (GPC) was then used as a further clean up before quantification by HRGC/HRMS. Quality control samples consisted of a trip blank for each site, a lab dialysis blank, a lab matrix spike, and a lab procedural blank. Water samples were collected at the beginning and end of each deployment to measure total organic

carbon (TOC), dissolved organic carbon (DOC), and specific conductivity.

Due to preliminary results from Rumford, the Jay samples were analyzed differently. The chromatograms for the Rumford deployment had numerous interferents causing quantification problems such as concentration over-estimation or, conversely, non-detection. The physical clean up and the two-stage 24 hour dialysis remained the same. However, the dialysates were combined into composite samples of 5 SPMDs each resulting in an N=8 for each site. Also, the PCB standards were not injected because PCBs are a known interferent during dioxin/furan quantification. The same acidified silica gel slurry and GPC method were performed on the samples, but a fractionation with ENVI-carb reversible tubes from Supelco, Bellafonte, PA was utilized to ensure a better clean up of the samples. The same quality control was performed for the Jay samples.

Results

The results from the 2001 field season were calculated as nanogram of dioxin/furan per kilogram of SPMD. Estimated dissolved dioxin/furan concentrations in the river have yet to be determined for each of the sites. The coefficient of variation (CV) for the Rumford deployment ranged from 29 to 368% with an average of 92% for all the congeners. The Rumford data are not yet completed (12 of the 40 still have not been quantified). Most of the variation from Rumford originates from an ineffective clean up procedure and laboratory inexperience. The CV for the Jay deployment ranged from 9 to 115% with an average of 42%. However, after removing one statistical outlier (> 2 standard deviations from the mean) from the upstream data and two downstream samples that didn't satisfy EPA Method 1613 quality assurance, the CV ranged from 6% to 38% with an average of 18%. Both data sets have a co-eluting peak with 2,3,7,8-TCDD leading to quantification problems for that congener. The toxic equivalency values (DTE) were determined using the World Health Organization's toxic equivalency factors for mammals.

Concentrations of most congeners were lower below the mills than above (Figures 1 and 2). The comparison between the 2000 and 2001 Rumford deployments show distinct similarities in congener profile for the population of samples with the exception of less non-detections in the 2001 data. However, with the amount of variability present in each set of samples, more validation is needed for that site.

Objectives for 2002

1. Reduce the variability between replicates to facilitate development of a more sensitive A/B test. A coefficient of variation of ~20% is expected.

2. Use PRCs as an *in situ* calibration for varying environmental conditions such as water velocity, temperature, and biofouling.

3. Develop a deployment scheme to eliminate possible vandalism and other logistical problems.

4. Perform a method detection limit study with composites of 4 SPMDs.

Conclusions

Of all the test types (large and small bass, large sucker filets and whole fish, sucker liver composites, freshwater mussels, and SPMDs) tested since 1997, only the fish and livers were able to detect significant differences between stations above and below some bleached kraft pulp and paper mills. MSDs were generally lower for mature or juvenile bass or for suckers depending on station, contaminant and year, but none have attained or consistently approached the goal of an MSD of 10% of background concentrations. SPMDs have not performed as well as fish, but new sampling design and cleanup techniques promise better results. These devices will be tested again along with fish in 2002.

Figure 1. DTE values for 2001 deployments.

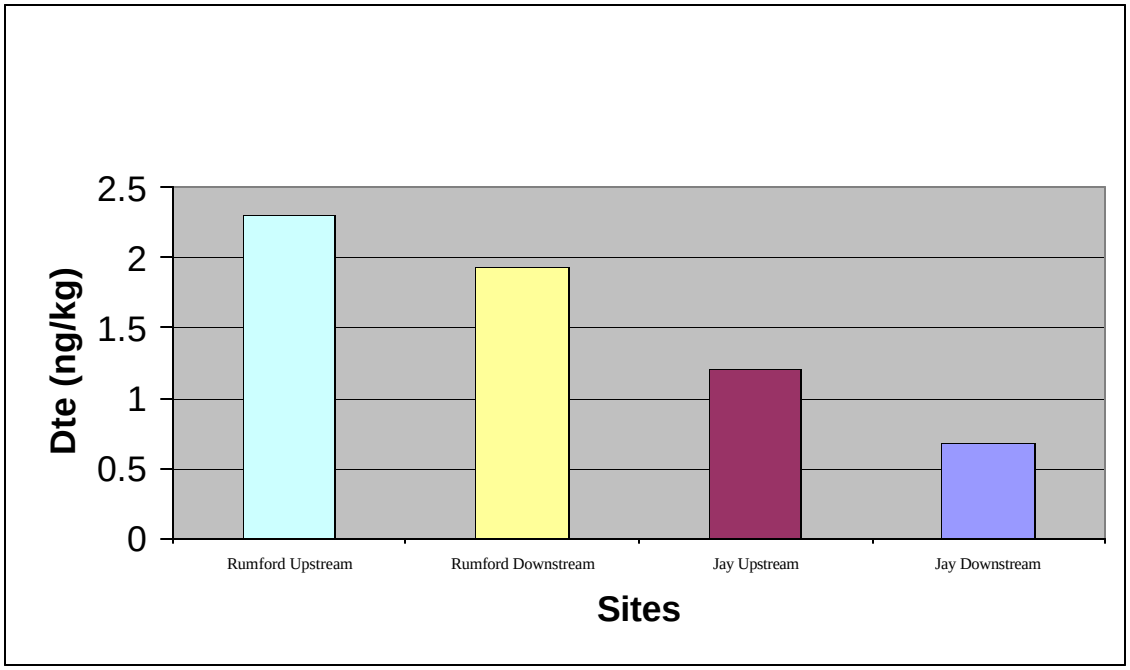
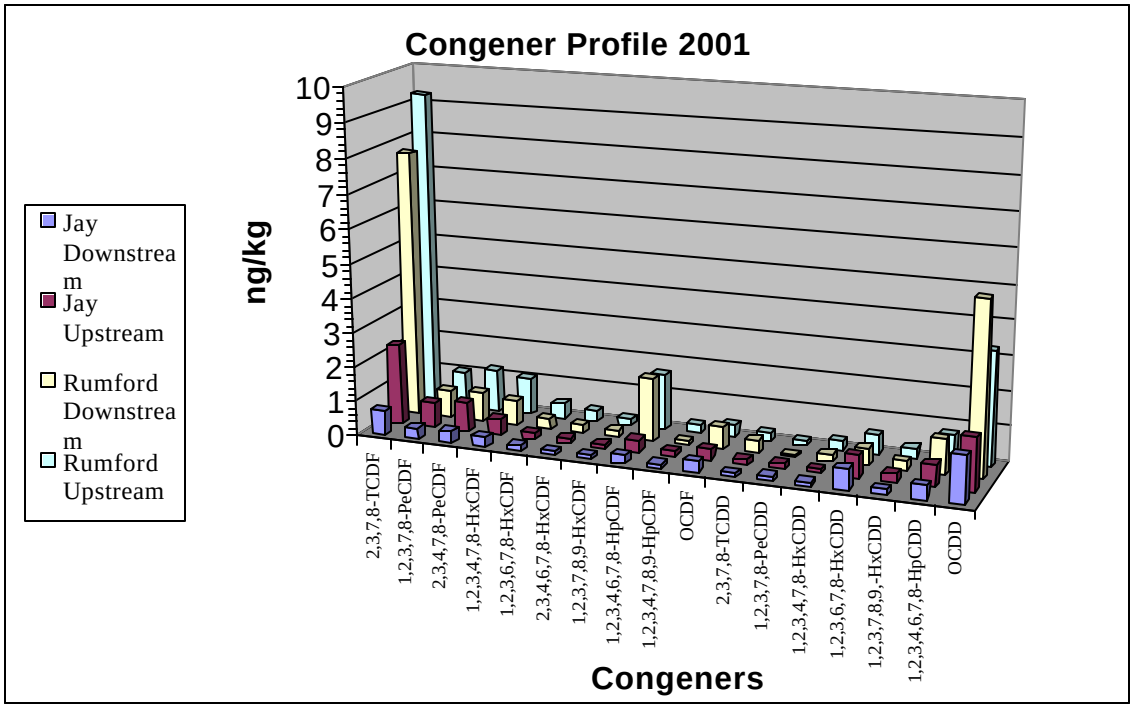


Figure 2. Congener Profile for the 2001 deployments.



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APPENDIX 1

MAINE BUREAU OF HEALTH

FISH CONSUMPTION ADVISORY, AUGUST 2000

LOBSTER TOMALLEY CONSUMPTION ADVISORY, 2 FEBRUARY 1994

Fish and shellfish consumption advisories can be seen at the Maine Bureau of Health's Environmental Toxicology Program website at http://www.state.me.us/dhs/etp/fca.htm

APPENDIX 2

DIOXIN AND FURAN CONCENTRATIONS IN 2001 FISH SAMPLES

CODES	STATIONS
AGL	ANDROSCOGGIN RIVER AT GILEAD
ARP	ANDROSCOGGIN RIVER BELOW GILEAD AT RUMFORD POINT
ARF	ANDROSCOGGIN RIVER BELOW RUMFORD
ARY	ANDROSCOGGIN RIVER AT RILEY
ALV	ANDROSCOGGIN RIVER AT LIVERMORE FALLS
AGI	ANDROSCOGGIN RIVER AT GULF ISLAND POND, AUBURN
ALS	ANDROSCOGGIN RIVER AT LISBON FALLS
ALW	ANDROSCOGGIN LAKE AT WAYNE
KMD	KENNEBEC RIVER AT MADISON
KNW	KENNEBEC RIVER AT NORRIDGEWOCK
KFF	KENNEBEC RIVER AT SHAWMUT, FAIRFIELD
KSD	KENNEBEC RIVER AT SIDNEY
KAG	KENNEBEC RIVER AT AUGUSTA
PBG	PENOBSCOT RIVER AT GRINDSTONE
PBR	PENOBSCOT RIVER W BR AT EAST MILLINOCKET
PBW	PENOBSCOT RIVER AT WOODVILLE
PBM(PBN)	PENOBSCOT RIVER AT WINN
PBL	PENOBSCOT RIVER AT SOUTH LINCOLN
PBC	PENOBSCOT RIVER AT MILFORD
PBV	PENOBSCOT RIVER AT VEAZIE
PBB	PENOBSCOT RIVER BELOW BANGOR AT ORRINGTON
PWD	PRESUMPSCOT RIVER AT WINDHAM
PWB	PRESUMPSCOT RIVER AT WESTBROOK
SFA	SALMON FALLS RIVER AT ACTON
SFS	SALMON FALLS RIVER AT SOUTH BERWICK
SEC	SEBASTICOOK RIVER E BR AT CORINNA
SEN	SEBASTICOOK RIVER E BR AT NEWPORT
SLN	SEBASTICOOK RIVER AT NEWPORT
SWH	SEBASTICOOK RIVER W BR AT HARTLAND
SWP	SEBASTICOOK RIVER W BR AT PALMYRA
SCW	ST CROIX RIVER AT WOODLAND
SCB	ST CROIX RIVER AT BARING

SPECIES

BNT	BROWN TROUT
CHP	CHAIN PICKEREL
LMB	LARGEMOUTH BASS
SMB	SMALLMOUTH BASS
WHP	WHITE PERCH
WHS	WHITE SUCKER

APPENDIX 3

TCDD AND TCDF IN SLUDGE FROM MAINE WASTEWATER TREATMENT PLANTS

APPENDIX 4

TCDD AND TCDF IN EFFLUENT FROM MAINE WASTEWATER TREATMENT PLANTS

APPENDIX 5

2378-TCDD AND 2378-TCDF IN SEDIMENTS

FROM VARIOUS STATIONS ON THE ANDROSCOGGIN RIVER

APPENDIX 6

SAMPLE LOCATION MAPS

APPENDIX 7

LENGTHS AND WEIGHTS

IN 2001 FISH SAMPLES

APPENDIX 8

SAMPLING SCHEDULE FOR THE 2001 DIOXIN MONITORING PROGRAM

Sampling schedule for the Dioxin Monitoring Program

May (early stations)

Androscoggin R at Lisbon Falls for brown trout
Kennebec R above Madison for brown trout
Kennebec R at Augusta for brown trout
Kennebec R at Fairfield for brown trout

E Br Sebasticook R at County Rd, Newport for bass/wh perch
W Br Sebasticook R at Rt 2 Palmyra for bass

JULY-AUGUST (all rivers in order, beginning at upstream stations)

Androscoggin R - July
Kennebec R - July
Penobscot R - August
Presumpscot R - August
Salmon Falls R - August
Sebasticook R (East and West Branches) - August

APPENDIX 9

TOXIC EQUIVALENCY FACTORS FOR PCDDS AND PCDFS

Appendix 9. Toxicity Equivalency Factors for PCDDs AND PCDFs (Van den Berg et al, 1998)

Congener	**Toxic Equivalency Factor (TEF)**		
	Humans/ Mammals	**Fish**	**Birds**
Dioxins			
2,3,7,8-TCDD	1	1	1
1,2,3,7,8-PeCDD	1	1	1
1,2,3,4,7,8-HxCDD	0.1	0.5	0.05
1,2,3,6,7,8-HxCDD	0.1	0.01	0.01
1,2,3,7,8,9-HxCDD	0.1	0.01	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.001	<0.001
OCDD	0.0001	<0.0001	0.0001
Furans			
2,3,7,8-TCDF	0.1	0.05	1
1,2,3,7,8-PeCDF	0.05	0.05	0.1
2,3,4,7,8-PeCDF	0.5	0.5	1
1,2,3,4,7,8-HxCDF	0.1	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01
OCDF	0.0001	<0.0001	0.0001
PCBs			
3,4,4',5-TCB (81)	0.0001	0.0005	0.1
3,3',4,4'-TCB (77)	0.0001	0.0001	0.05
3,3',4,4',5-PeCB (126)	0.1	0.005	0.1
3,3',4,4',5,5'-HxCB (169)	0.01	0.00005	0.001
2,3,3',4,4'-PeCB (105)	0.0001	<0.000005	0.0001
2,3,4,4',5-PeCB (114)	0.0005	<0.000005	0.0001
2,3',4,4',5-PeCB (118)	0.0001	<0.000005	0.00001
2',3,4,4',5-PeCB (123)	0.0001	<0.000005	0.00001
2,3,3',4,4',5-HxCB (156)	0.0005	<0.000005	0.0001
2,3,3',4,4',5'-HxCB (157)	0.0005	<0.000005	0.0001
2,3',4,4',5,5'-HxCB (167)	0.00001	<0.000005	0.00001
2,3,3',4,4',5,5'-HpCB (189	0.0001	<0.000005	0.00001

APPENDIX 10

DIOXIN AND FURAN IN FISH AND SHELLFISH 1984-1996

APPENDIX 11

SPMD DATA